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CHEMICAL ANALYSIS OF THE DYES USED IN NAVY GREEN AND
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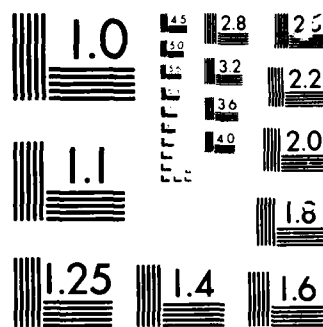
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CHEMICAL ANALYSIS OF THE DYES USED IN NAVY GREEN AND YELLOW COLORED SMOKES

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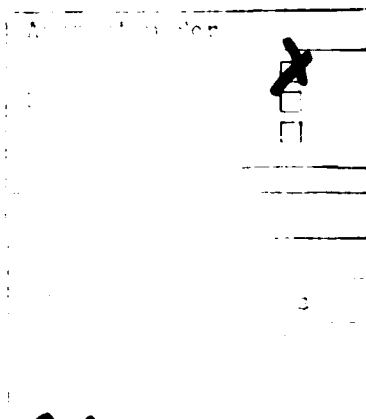
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<p>This paper provides the results of a complete qualitative analysis on the commercial green and yellow dyes, including the side products formed in the manufacturing process. The investigative techniques included gas chromatography (GC), gas chromatography/mass spectroscopy (GC/MS), nuclear magnetic resonance spectroscopy (NMR), liquid chromatography (LC), thin layer chromatography (TLC), atomic absorption spectroscopy (AA) and energy dispersing x-ray analysis (EDXA).</p>					
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SUMMARY

The organic dyes used in Navy green and yellow colored smokes can contain up to 23% unknown/undefined impurities. These impurities may be hazardous by themselves, or may form hazardous products after combustion. In some cases, they may also affect the burning rate and burning efficiency of the colored smokes.

This paper provides the results of a complete qualitative analysis on the aforementioned green and yellow dyes, including the side products formed in the manufacturing process. The investigative techniques included gas chromatography (GC), gas chromatography/mass spectroscopy (GC/MS), nuclear magnetic resonance spectroscopy (NMR), liquid chromatography (LC), thin layer chromatography (TLC), atomic absorption spectroscopy (AA) and energy dispersing x-ray analysis (EDXA). *Page 12*



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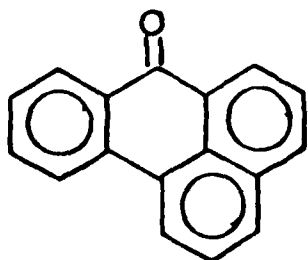
I. INTRODUCTION

In the fiscal years 1981 to 1984, we reported the identification of combustion products which were the results of burning three organic dyes in the green colored smoke devices (two dyes in yellow colored smokes).¹⁻⁴ Initially, we did not consider the fate of the organic impurities in the dyes; however, since they contain a significant amount of impurities (10-20 percent), it may be important to include in our studies the major impurities of the dyes and their combustion products found in the effluent.

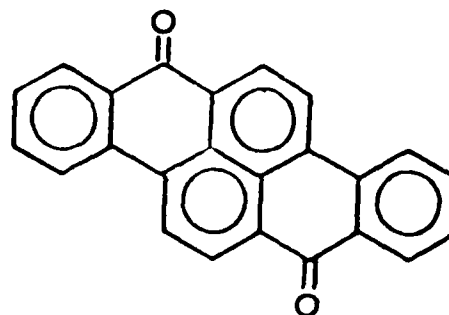
The three dyes used in the green colored smoke compositions are benzanthrone, Vat Yellow 4 and Solvent Green 3. The first two dyes are also used in the yellow colored smoke compositions. A typical colored smoke device contains approximately 44% dye mixture, 23% fuel (sugar), 29% oxidizer (potassium chlorate), 2% cooling agent (sodium bicarbonate) and 2% binder (diatomaceous earth). The chemical structures of the dyes are shown in Figure 1.

The lot acceptance, development/performance test as well as surveillance test plans require that test samples be periodically drawn from new and retail stocks for quality assurance tests. Such tests, including the T&H test (temperature and humidity) and the burning of the conventional and newly formulated devices, are performed by Naval Weapons Support Center, Crane. It was found that burning rate of some of the colored smoke devices after T&H test (-65°F and 160°F at 95% relative humidity for 14 to 28 days) could not meet the required specification. The reason for this high reduction in burning rate is probably due to the fact that the dyes or the large number of impurities in the dyes deteriorate the physical and chemical properties of the colored smoke composition.

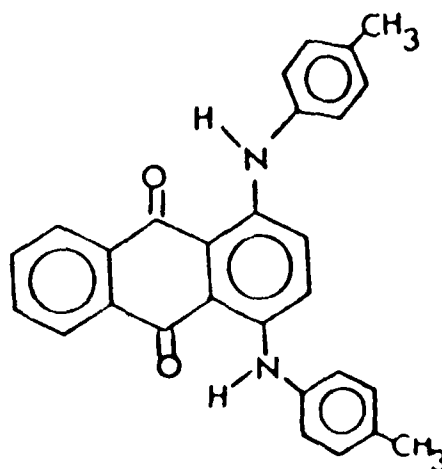
The purpose of this paper is to provide the information of the major impurities in the dye mixture which may produce hazardous emissions, or may affect the burning character during functioning.



Benzanthrone
7, oxo 7-benz(d,e)anthraquinone
m.p. = 174°C
m.w. = 230
yellow



Vat Yellow 4
dibenzo(a,h)pyrene 7,14-dione
m.p. = 385°C
m.w. = 332
yellow



Solvent Green 3
1,4-di-p-toluidinoanthraquinone
m.p. = 218°C
m.w. = 418
green-blue

Figure 1. Chemical Dyes used in Green and Yellow Colored Smoke Devices.

II. EXPERIMENTAL

Samples

Samples of benzanthrone, Vat Yellow 4 were received from two different manufacturers. Samples of Solvent Green 3 were from only one source.

Thin Layer Chromatograph Analysis (TLC)

The dye samples were dissolved in acetone. The acetone solutions were then applied to a 500 μ m silica gel TLC plate. The plate then was eluted with a solution of 50:50 xylenes and chloroform and R_f values noted.

High Performance Liquid Chromatograph (HPLC)

The dye samples were dissolved in methanol. The methanol sample was then injected onto a RP-18 LiChrosorb column (25 cm long, 1/4 inch outside diameter, 5 μ m particle size) and eluted with 100 percent methanol (Flow rate = 2 ml/min.) on a Hewlett-Packard 1080A HPLC instrument. The HPLC chromatograms of benzanthrone, Vat Yellow 4 and Solvent Green 3 are shown in Figures 2-4, respectively.

Gas Chromatograph/Mass Spectrometer (GC/MS) Analysis

The three dye samples (and samples separated by TLC and HPLC) were analyzed by DuPont DP-102 GC/MS/DS System. The directed probe temperature was programmed from 50-250°C at 20°C/min. The mass spectrum of the soluble material of the as-received dye samples from Atlantic Richfield Co. are shown in Figures 5-7, respectively.

Nuclear Magnetic Resonance (NMR) Spectroscopic Analysis

The three dye samples and some major samples separated by TLC and HPLC were analyzed by Nicolet 60 MHz, 270 MHz and 500 MHz Fourier Transform NMR System. Samples were dissolved in deuterated chloroform and deuterated dimethylsulfoxide. Tetramethylsilane is the internal standard. NMR spectrum for the three dyes are shown in Figures 8-10, respectively.

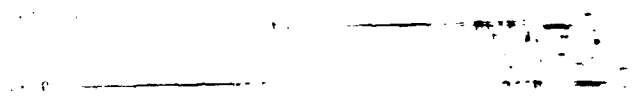


Figure 2. As-Received methanol; flow rate, 2 ml/min; on a Hewlett Packard 1080A HPLC instrument using a BP-18 column.

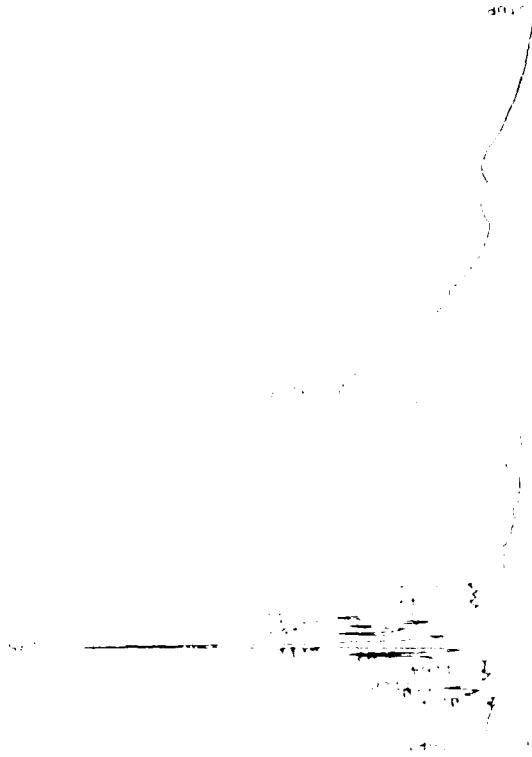


Figure 3. As-Received yellow 4 showing impurities. Solvent, methanol; mobile phase, 100% methanol; flow rate, 2 ml/min; on a Hewlett Packard 1080A HPLC instrument using a BP-18 column.

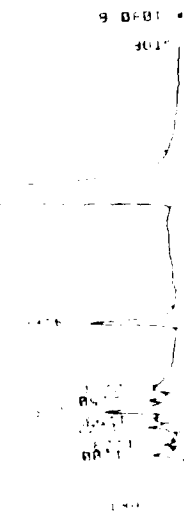


Figure 4. As-Received solvent green 3. Solvent, methanol; mobile phase, 100% methanol; flow rate, 2 ml/min; on a Hewlett Packard 1080A HPLC instrument using a BP-18 column.

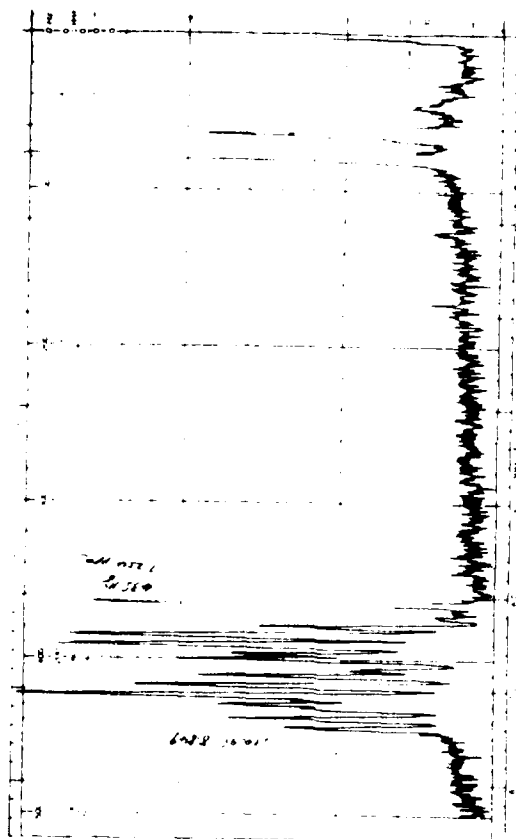


Figure 9 NMR Spectrum of Benzothione in $CDCl_3$. Tetramethylsilane is the internal standard.

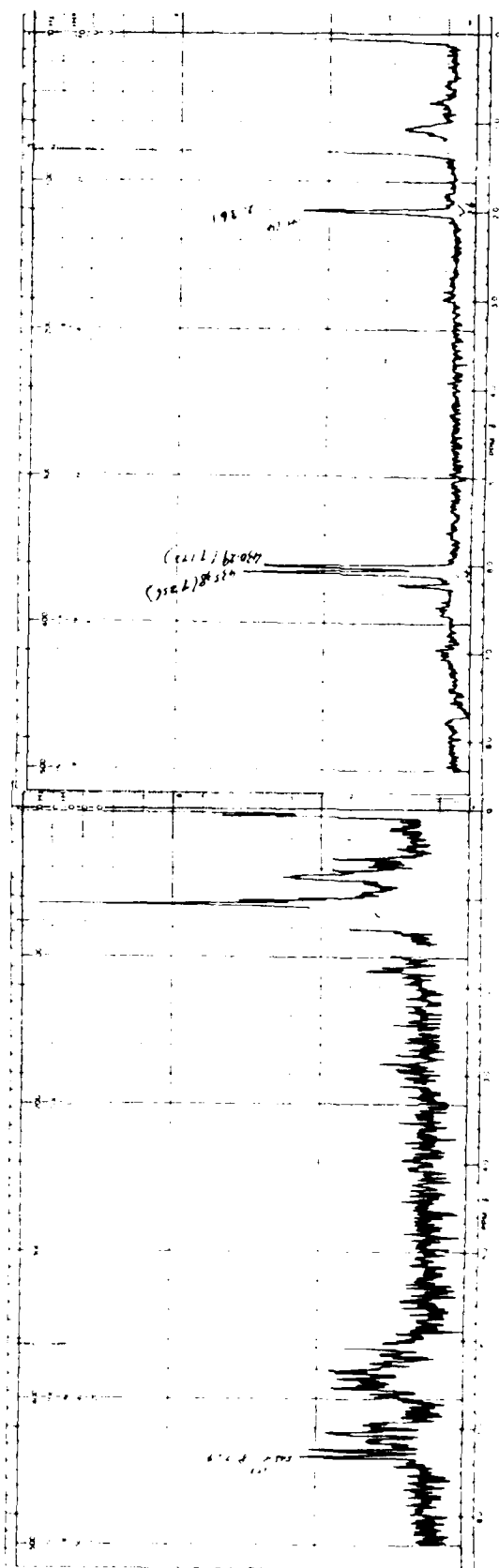


Figure 10 NMR Spectrum of 3-(trimethylsilyl)propionic acid, sodium salt, in $DMSO-d_6$. Tetramethylsilane is the internal standard.

Figure 11 NMR Spectrum of 3-(trimethylsilyl)propionic acid, sodium salt, in $DMSO-d_6$. Tetramethylsilane is the internal standard.

Energy Dispersive X-ray (EDXA) Analysis

This analysis was done using a Kevex System 7000 EDXA and Amray Model 1600 SEM. A powdered dye sample was glued on an aluminum stud coated with carbon powder and scanned by x-ray. Elements with different core electron binding energies would be dispersed and showed at different energy position (e.v.) on the spectrum. Results of this analysis are listed in Table 1.

III. RESULTS AND DISCUSSIONS

Benzanthrone

Samples of benzanthrone were received from two different manufacturers and have been analyzed by TLC, HPLC, MS, and EDXA. Both of the samples contain approximately 5-6 mg of black insoluble material in every 50 mg of the crude sample. The approximate percentage composition of the as-received benzanthrone samples is shown in Table 2 (\pm 3% error).

Most benzanthrones seemed to be contaminated by very little amount of Vat Yellow 4 and 1-chloro-Vat Yellow 4, this probably due to the transfer of benzanthrone by an unclean spatula. The impurity at m/e 408 contains only one carbonyl group. It is clear this must be a higher molecular wt. hydrocarbons with benzanthrone as its basic backbone. The difference between m/e 408 and 230 is 178, which is the molecular weight of anthracene. This means an anthracene type of hydrocarbon is attached on the benzanthrone which leads to the compound with molecular weight m/e 408. The exact connection between those two needs more studies.

1-(or 5-)hydroxy benzanthrone is the major soluble impurity. Since the heat generated during the combustion of a smoke device can only break the side chains of an aromatic compound, the only possible combustion product of the hydroxy benzanthrones can be benzanthrone. We observed that most of the hydroxy benzanthrones remained even after combustion.

TABLE 1. EDXA RESULTS OF BENZANTHRONE, VAT YELLOW 4 AND SOLVENT GREEN 3

<u>Element</u>	<u>benzanthrone</u>	<u>Vat Yellow 4</u>	<u>Solvent Green 3</u>
Al	s	s	m
Si	m	s	m
Cl	m	s	s
Fe	m	s	t
K	m	m	t
Zn	t	m	t
S	m	m	m
Br	t	t	t
pb	t	t	t
Na	m	m	m

Quantification is estimated by the peak intensities.

l = large, s = small, m = moderate, t = trace

TABLE 2. THE APPROXIMATE COMPOSITION OF THE AS-RECEIVED BENZANTHRONE*
SAMPLES FROM TWO MANUFACTURERS

<u>Sample Source</u>	<u>Percent Benzanthrone</u>	<u>Percent 1-(or 5-)-hydroxy Benzanthrone</u>	<u>Percent Insoluble Material**</u>	<u>Percent Other</u>
Atlantic Chemical	85	2	11	2
Carey	79	5	12	4

* The minimum acceptable purity in Mil-Spec is 77 .

** CCl₄ was used as the solvent.

Since the ionization % of hydroxy- or amine- type of compounds in the mass spectrometer is very low, the intensity of the parent peak (molecular ion peak) is usually weaker than that of compounds without such functional groups. It will, therefore, not be appropriate to depend on that to compare the % yield or % purity between two compounds. It is suggested that HPLC (U.V. detector) should be used for these compounds, although the maximum absorption and absorption coefficient for different type compounds may make the results inaccurate.

The insoluble fraction contains black tar, iron, and non-combustible (maybe sodium sulfate) as well as some dehydrated glycerol resin polymers (aromatics) and dextrin as diluent. Table 1 shows the elements contained in the insolubles. The values reported as Percent Other include volatiles and any experimental errors. Upon burning, the dehydrated glycerol resin polymers produce lower molecular weight resins which are observed in the effluent. The volatile organic species are probably burned to carbon dioxide, carbon monoxide, hydrogen, etc., since they have not been recovered in the products per se.

Vat Yellow 4

Since only H_2SO_4 can completely dissolve Vat Yellow 4, the HPLC method should not be used to determine the % purity (*a little H_2SO_4 in the HPLC column will destroy the packing material). We used methanol to substitute for H_2SO_4 , and the spectrum should be used only as a reference for impurities in the Vat Yellow 4.

The MS study indicated that monochloro-Vat Yellow 4 is the major impurity in the dye, therefore, MS is alright to be used as a tool for the % purity studies. It is believed that the ionization % between Vat Yellow 4 and its chloro derivative are close enough.

The only possible major combustion product which can be produced from burning chlorinated Vat Yellow 4 in these devices is Vat Yellow 4 itself.

A study of the mass spectrum of the combustion products of Vat Yellow 4 shows that most of the chlorinated Vat Yellow 4 remains unchanged. The insoluble materials are mostly dextrin and inorganic salts such as aluminum chlorohydrate and aluminum hydroxide which were the by-products of the work-up procedures for the preparation of the dye. The volatile organic species are probably burned to carbon dioxide, carbon monoxide, hydrogen, etc., since they have not been recovered in the products per se. Table 1 also shows the elements contained in the insolubles. The analytical data of as-received Vat Yellow 4 from two different sources are shown in Table 3 ($\pm 3\%$ error).

Solvent Green 3

There is only one manufacturer for the Solvent Green 3 dye. The purity is around 91 percent. Analysis indicates that the major impurity is the antidusting oil (straight chain hydrocarbons) which is converted to lower molecular weight hydrocarbons upon combustion. The other minor impurities are some low molecular weight organic species which are probably starting materials used in the synthetic procedures, and some products from degradation of Solvent Green 3 dye itself. The inorganic impurities are shown as elements in Table 1.

The analytical data of as-received Vat Yellow 4 are listed in Table 4 ($\pm 2\%$ error).

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TABLE 3. THE APPROXIMATE COMPOSITION OF THE AS-RECEIVED
VAT YELLOW 4 SAMPLES*

Sample Source	Percent Vat Yellow 4	Percent Monochloro	Percent Dichloro	Percent** Insoluble and Others
Atlantic Chemical	86	10	1	3
Carey	83	13	1	3

* The minimum acceptable purity in Mil-Spec is 80%.

** Solvent = CH_3OH .

TABLE 4. THE APPROXIMATE COMPOSITION OF THE AS-RECEIVED
SOLVENT GREEN 3 DYE*

Sample Source	Percent Solvent Green 3	Percent Antidusting Agent	Percent** Solubles	Percent Insoluble and Others
Atlantic Chemical	94	2	2	2

* The minimum acceptable purity in Mil-Spec is 90%.

** Solvent = acetone.

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